Working under relative and absolute humidity with DSC, calorimetry, TGA and TMA techniques

INTRODUCTION

The requirements for thermal analysis under humid atmosphere with a specific humidity are increasing and the conditions are diverse and related to different fields of applications: influence of the humidity on a chemical process (reaction, degradation…), moisture adsorption on a solid sorbent, plasticization effect, metallic corrosion, coal gasification…
Most of the thermal analysis (DSC, TGA, TMA) and calorimetric techniques are easily adaptable to investigate the effect of humidity on a given material however the first variable to be considered is if relative or absolute humidity has to be used for the test.

As the definition of this parameter is very often confusing, a first part will give an explanation about humidity and the different specific parameters related to humidity.

DEFINITION OF HUMIDITY, RELATIVE AND ABSOLUTE HUMIDITY

Humidity
Humidity is defined as the amount of water vapour in a gas (air for example). Humidity can be measured using a hygrometer. But humidity is normally measured as relative humidity (RH). The first step of which is needed to define the water vapour pressure.

Saturated water vapour pressure
The saturated water vapour pressure is the pressure corresponding to the saturation of the water vapour. The water vapour pressure is the partial pressure of water vapour in any gas mixture saturated with water. The saturated water vapour pressure varies with temperature (see figure 1).

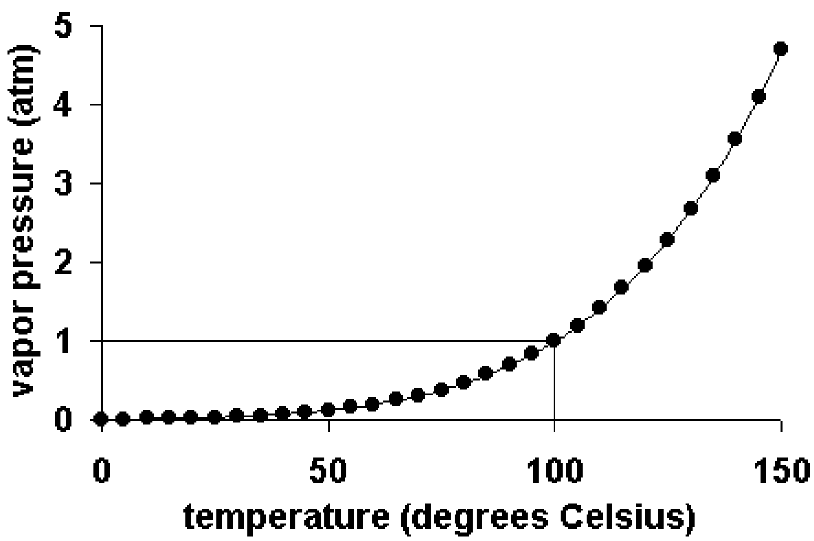


Figure 1: Variation of the water vapour pressure versus temperature

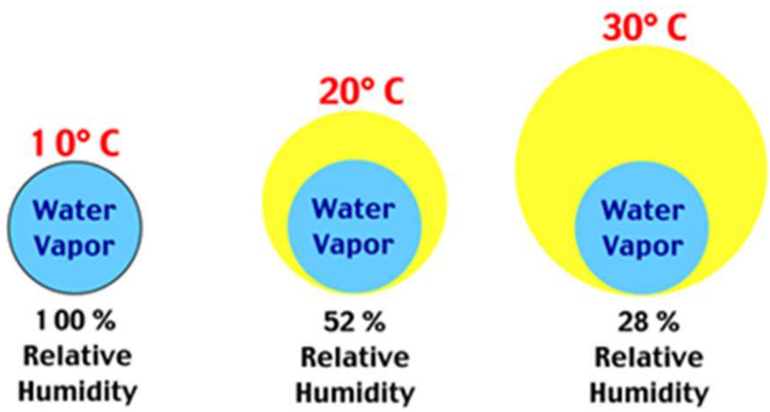
Relative humidity

Relative humidity is expressed in ratio that indicates the amount of moisture (water vapour) in the gas relative to the maximum amount the gas can hold at that temperature, or expressed in a different way, the ratio of the partial pressure of water vapour, P_{vap}, to the theoretical saturated water vapour pressure $P_{vap}(T)$ expressed in percentage at a given temperature . It is expressed as:

$$\varphi\,[\%] = \frac{P_{\text{vap}}}{P_{\text{sat}}(T)} \times 100$$

The ratio RH varies with the temperature and the pressure variations.

As an example (see following figure), suppose that air is saturated at 10°C that is to say the relative humidity is 100%. When the air temperature increases to 20°C or 30°C, more volume is available each time for the water vapour. As the amount of water vapour remains constant, as a consequence the RH value decreases. It can also be said that warmer air can hold more water vapour



Absolute humidity

Absolute humidity is the amount of water vapour in the gas. It is limited by the maximum amount that the gas can absorb before reaching the saturation at a given temperature. Absolute humidity is expressed in gH_2O per.$m^{-3}$of gas or gH_2O per kg of gas. For example, when air is saturated at 30° C, absolute humidity is about 30g.m^{-3}.

The figure 2 shows that it is possible to compare relative humidity and absolute humidity according to temperature. The diagram allows to notice:

- for a selected temperature, the amount of water in air (absolute humidity) increases when the RH increases
- an amount of water in air (absolute humidity) equal to 20 gH_2O per kg of gas, is obtained at 25° C/100%RH and 35° C/50%RH.

Wetsys (RT to 70°C)

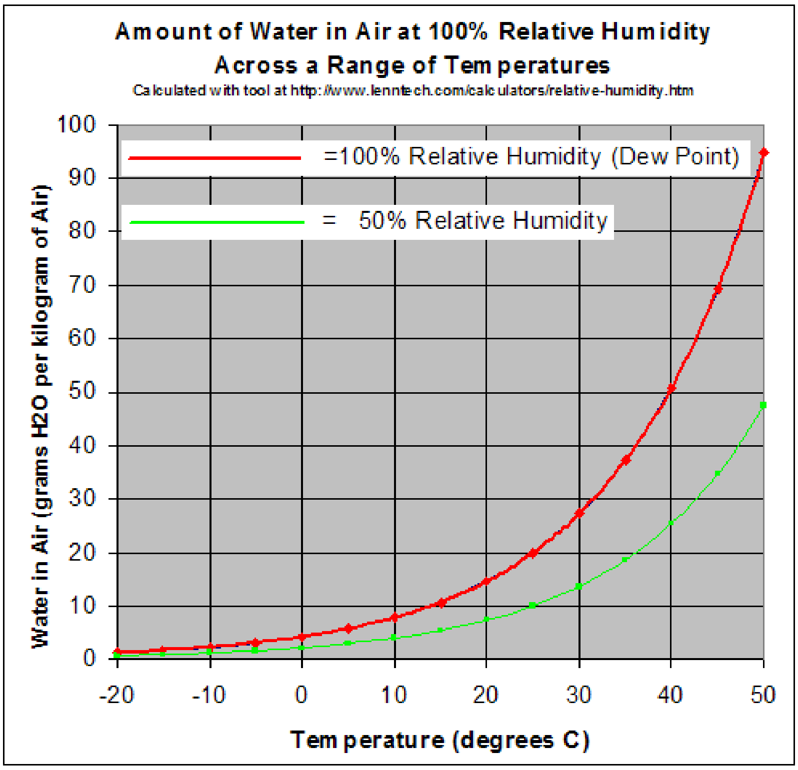


Figure 2: Variation of the absolute humidity versus temperature at different relative humidities

Dew point

Another important parameter to be defined is the dew point. The dew point temperature is the temperature at which the water vapour pressure is equivalent to the saturated water vapour. It is also the temperature below which the water vapour in a volume of humid gas at a constant pressure will condense into liquid water.

The dew point is related to relative humidity as seen on the following figure 3:

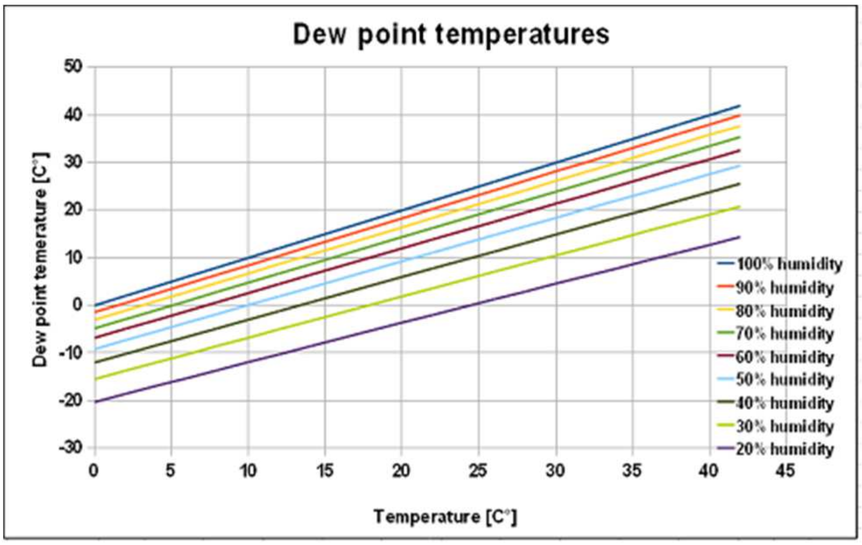


Figure 3: Variation of the dew point temperature versus temperature and relative humidity

Wetsys
(RT to 70°C)

It is also possible to combine all the parameters: relative humidity, absolute humidity and dew point, on a single diagram called Mollier diagram (see figure 4).

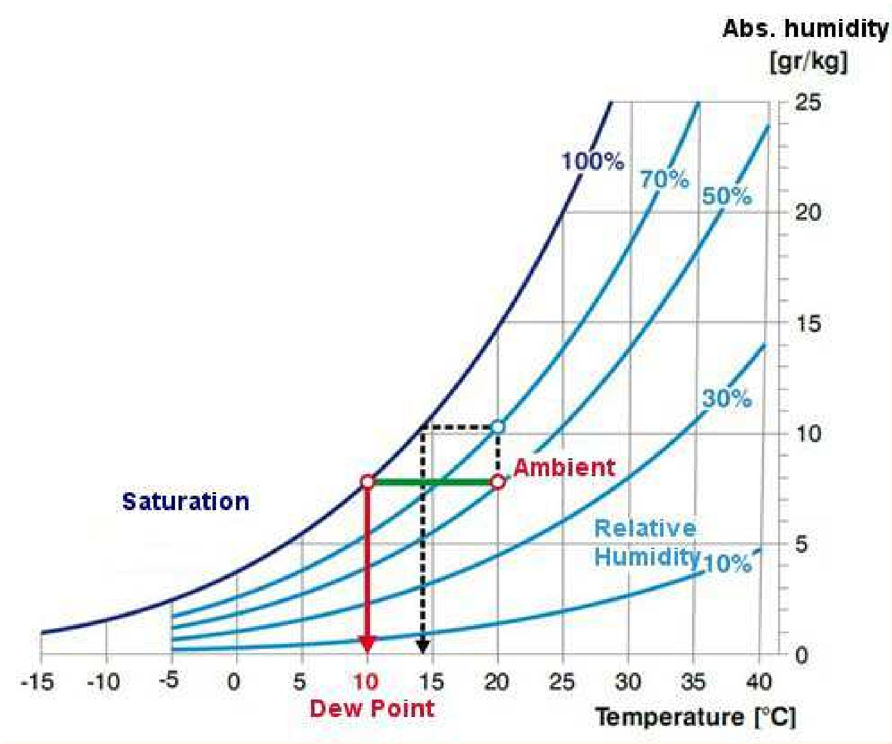


Figure 4 : Mollier diagram

For example for air at 20°C with a 50%RH, if the temperature of air decreases, condensation will appear around 10°C. If the relative humidity is higher, the dew point temperature will also increase.

WETSYS: THE RELATIVE HUMIDITY GENERATOR

Description

WETSYS is designed for any application in which regulating the relative humidity rate of a chamber is necessary. WETSYS is a compact and automate wet gas generator that can be adapted on any thermal analyzer such as calorimeters, micro-calorimeters, TGA, TMA from the SETARAM instruments range. But it can also be adapted on any other scientific device of instrumentation for which regulation of atmosphere's relative humidity is required (microscopy, Raman spectroscopy, X-ray diffractometers…).

WETSYS is based on a simple principle: the mixing of a dry gas and a water-saturated gas so as to maintain the relative humidity of a gas at a given temperature as described on the following diagram (figure 5):

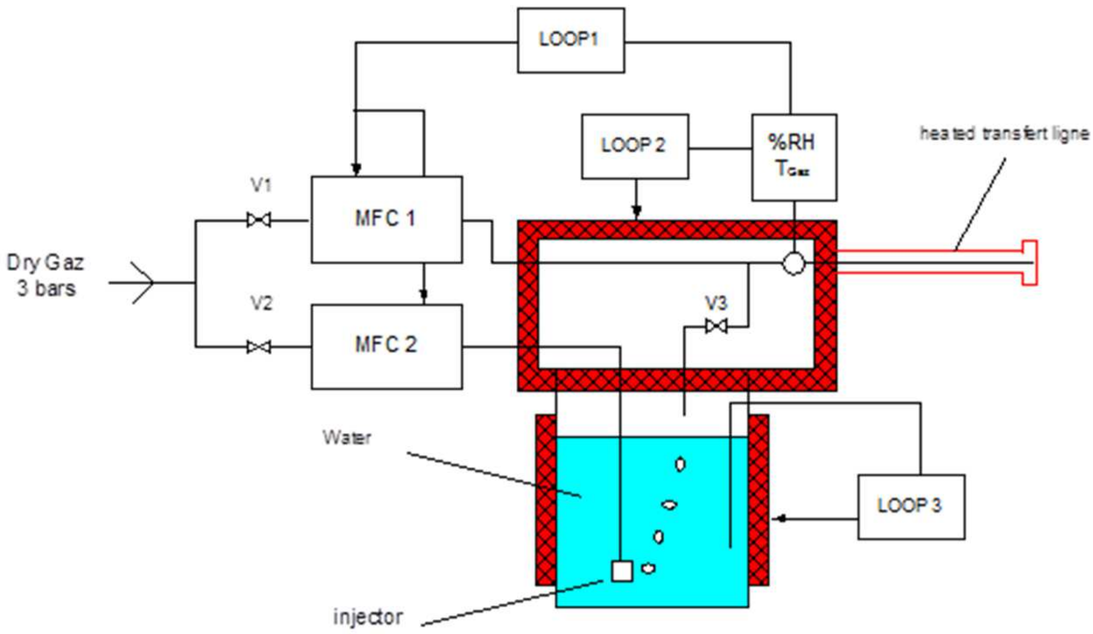


Figure 5: Wetsys principle

The dry gas at the inlet is divided in two paths: dry (MFC1) and wet (MFC2). These two paths are then combined and enter the humidity measurement chamber. The humidity probe enables the measurement and regulation of the relative humidity rate by retroaction on the two mass flow meters, while keeping a stable and constant flow rate.

The process controller manages three control loops:

- control of the relative humidity rate via two mass flow meters and the humidity probe (LOOP 1).
- control of the outlet gas temperature (LOOP 2).
- temperature control of the water in the evaporator (LOOP 3).

Wetsys
(RT to 70°C)

Measuring temperature and relative humidity is done via a ROTRONIC probe. This system gives a stability better than ±0.3% RH. A heated transfer line avoids any risk of condensation between the wet gas generator, WETSYS, and the thermal analyzer

In general, it is recommended to fix the control temperature of the heated transfer line at least 15 °C above the dew point of the wet gas generated. On connections, the non-heated zones may be a location of condensation points. By heating 15°C above dew point, condensation risks are highly reduced.

A user friendly interface is driven by a process controller. It makes possible, besides generating a gas with controlled temperature and humidity, choosing the gas (Air, N_2, He, CO_2…), programming the relative humidity profile (constant or variable RH), setting the flow rate, working with a dry gas only, isolating WETSYS in case of vacuum-purging of the connected analyzer.

Figure 6 : The Wetsys

Experimental

The range of operation for the Wetsys is from 0 to 95%RH at 70°C that corresponds to 0 to 187 g/m3, that will be the maximum absolute humidity to be used in the thermoanalyzer. In this case the maximum dew point temperature is 70°C.

Two types of experimentations have to be discussed: calorimetric and thermogravimetric tests

- calorimetric test under humidity (C80)
- thermogravimetric test under humidity (Setsys, Sensys TG-DSC)

In the case of a thermogravimetric device, it is needed to protect the balance with a low flow of dry gas (helium is recommended). The flow of humid gas is introduced from the bottom of the furnace and will exit at the top of the furnace

WETSYS-C80 ADAPTATION

To work out humid gas with C80, it is necessary to heat the gas circulation cell's head to avoid any condensation before sweeping the sample.

The WETSYS / C80 adaptation is an auxiliary thermostat made of a thermostated block and a power supply. The thermostated block is mounted on the C80 (figure 7). It replaces the standard insulating block mounted at the top of it. The maximum temperature is 75°C.

The experiment is done using the gas circulation vessel (maximum flowrate: 30 ml/min) and can only be performed in the isothermal mode. That means that it is possible to run isothermal experiments from RT to 70°C.

The experiment is operated in such a way:

- Select WETSYS total flowrate: between 3 and 30 ml/min.
- Fix the thermostated block temperature: +5 (for low RH) to 10°C (for high RH) above the maximum dew point generated by WETSYS (that means that if the dew point is equal to the maximum value of 65°C, it will be possible to start the isothermal calorimetric test at 75°C according to the RH concentration).
- Fix the temperature of the heated transfer line to 15°C above the maximum dew point generated by WETSYS.

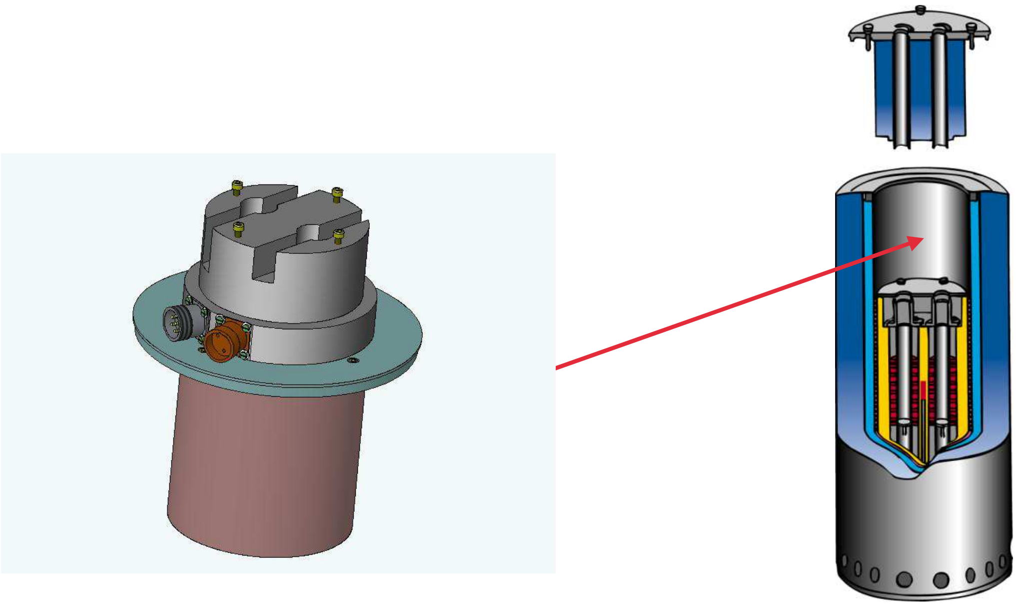


Figure 7: Auxiliary thermostat and C80 calorimetric block

It is important to sweep the sample with dry gas only (0%RH) at the beginning of the test to get a proper baseline prior to moisture interaction. Then the humidity is applied at a given RH using the step mode. In that case it is needed to wait for the stabilization of the humidity and the calorimetric signal.

Wetsys
(RT to 70°C)

WETSYS-SETSYS ADAPTATION

To work out with humid gas on SETSYS, it is necessary to heat the water in the circuit above the dew point generated by WETSYS. For this purpose it is needed to a dedicated chiller with a maximum temperature of operation equal to 80°C. Condensation is by that way avoided within the SETSYS furnace.

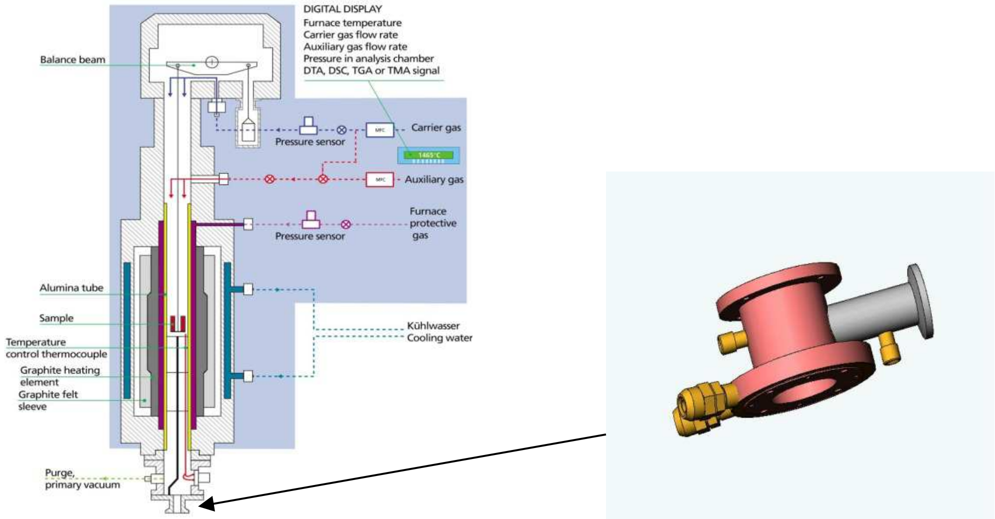


Figure 8 : Setsys diagram and thermostated bottom furnace flange

The thermostated bottom furnace flange (see figure 8) underneath replaces the standard flange. An insulated jacket is also added around the flange in order to improve the thermostatisation.

The experiment is operated in such a way:

- Operate vacuum in the furnace, the Wetsys status being OFF
- Fill the furnace with helium (carrier gas)
- Decrease the carrier gas flow to 10 ml/min and change status on the Wetsys to ON.
- Select WETSYS flowrate at 50 ml/min.
- Fix the water chiller temperature: +5 (for low RH) to 10°C (for high RH) above the maximum dew point generated by WETSYS (that means that if the dew point is equal to the maximum value of 70°C, the temperature of the chiller has to be at 80°C).
- Fix the temperature of the heated transfer line to 15°C above the maximum dew point generated by WETSYS

WETSYS-SENSYS TG-DSC ADAPTATION

To work out with humid gas in SENSYS TG-DSC furnace, it is necessary to heat the water in the furnace circuit above the dew point generated by WETSYS so that condensation phenomena are avoided within the furnace. For this purpose it is needed to a dedicated chiller with a maximum temperature of operation equal to 80°C. As the SENSYS TG-DSC is a symmetrical system, it is necessary to input humid gas in the two furnace's wells in order to keep symmetry due to buoyancy effect. For this purpose, a special heated interface was developed for the adaptation between WETSYS and SENSYS TG-DSC (see figure 9)

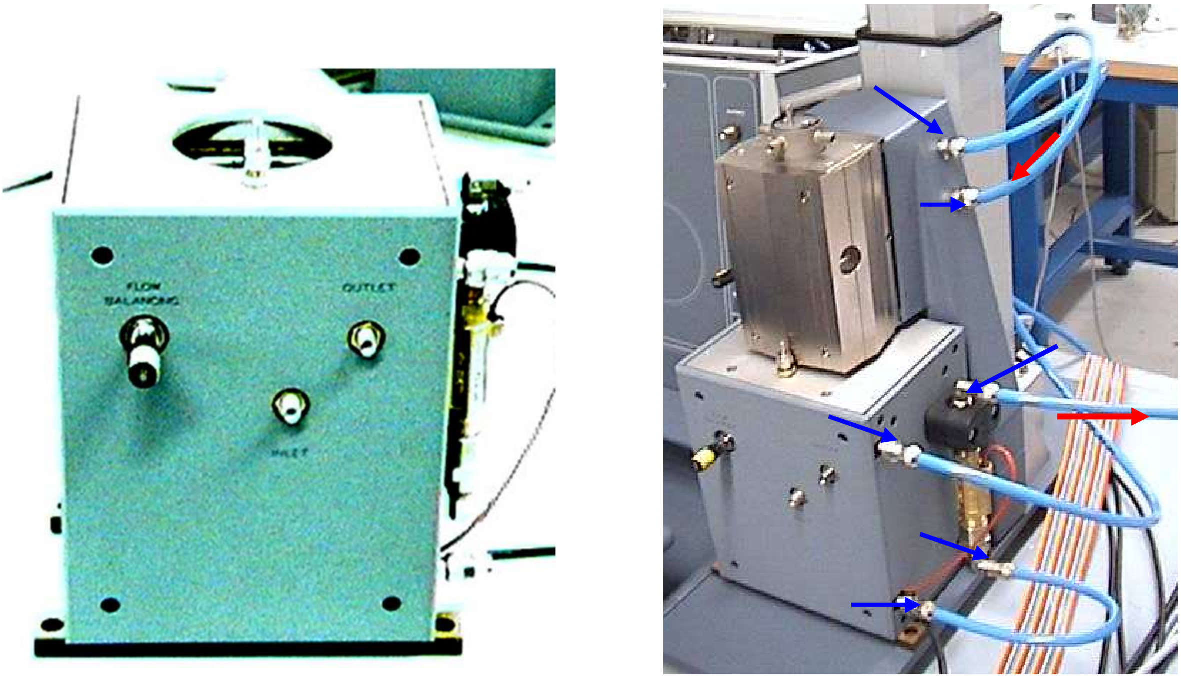


Figure 9: Special heated interface and adaptation on the Sensys

The experiment is operated in such a way:

- Operate vacuum in the furnace, the Wetsys status being OFF
- Fill the furnace with helium (carrier gas)
- Decrease the carrier gas flow to 10 ml/min and change status on the Wetsys to ON.
- Select WETSYS flowrate at 50 ml/min.
- Fix the water chiller temperature: +5 (for low RH) to 10°C (for high RH) above the maximum dew point generated by WETSYS (that means that if the dew point is equal to the maximum value of 70°C, the temperature of the chiller has to be at 80°C).
- Fix the temperature of the heated transfer line to 15°C above the maximum dew point generated by WETSYS